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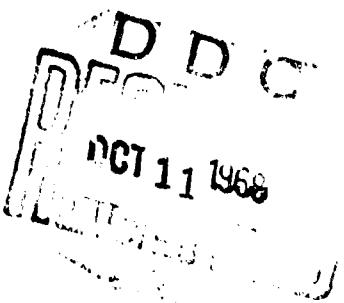
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THE DYNAMICS OF SORPTION

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The question of gas or vapor absorption from an air current by a sorbent is important in the design of gas masks and in the recuperation of solvent vapors. This problem, usually termed sorption dynamics, actually belongs in the field of chemical apparatus design. There is considerable experimental material on this question and a single attempt to construct a theory for the phenomenon, undertaken by Mecklenburg and Kubelka (Ref. 1). As will be shown later, their "theory" is pseudo-scientific and harmful in practical application. In the Soviet Union this theory has been developed in particular by Dubinin (Ref. 2), who considered several particular cases (chemical sorption (Ref. 3), sorption of mixtures, etc.) and used the theory without critical analysis in his text (Physicochemical Fundamentals of Sorption Technology), where it was presented as the "classical" (Ref. 3) theory of sorption dynamics. No critical analysis of this theory has been presented until recently. However, its analysis is particularly necessary since it cannot in any way be termed a physical theory, but is in essence a collection of errors and misunderstandings.

Let us examine the general pattern of sorption dynamic phenomena and introduce some necessary concepts and notations. Assume a tube with the cross-section S is filled with a porous sorbent, for example, activated charcoal with particle diameter d . A mixture of air with a substance to be absorbed begins to enter the tube at an instant of time which is taken as zero time. Assume that the substance concentration is C_0 and the velocity of the gaseous mixture is V liters/min. From the practical point of view, of greatest importance is the answer to the following question: after what time will there appear behind a sorbent layer of length L a definite

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concentration C_1 which can be measured by an instrument. For the case of a gas mask this phenomenon is known as breakthrough, and it is clear that the measuring instrument (indicator) must capture very small toxic concentrations of substances. The time from the moment of mixture entry to breakthrough is termed the screening effect time for the sorbent layer. Let us denote this quantity by the letter θ . Of primary interest in practice is the relation $\theta = f(L)$. Figure 1 shows experimentally determined curves (from the data of Zabozhinsky) showing this relation. We see from the figure that small values of θ correspond to small values of L ; for small values of θ the quantity $d\theta/dL$ is also small, i.e., the increase of θ for an increase of L is small.

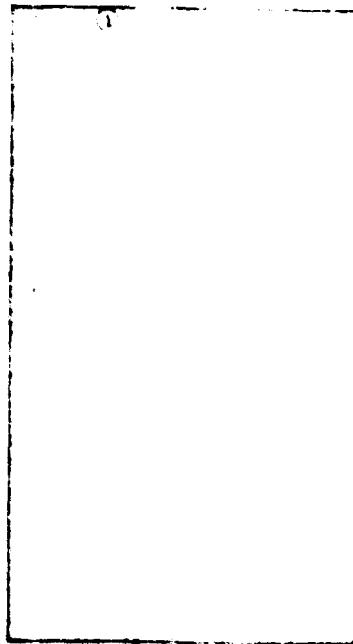


Fig. 1. Variation of screening effect time with length of activated charcoal layer for two velocities of air $\theta = f(L)$, $c = \text{const}$, $\alpha_1 > \alpha_2$

In a rough approximation we may consider that beginning at some point a , $d\theta/dL = \text{const}$, i.e., the function $\theta = f(L)$ becomes linear.

If we alter the concentration C_1 which corresponds to breakthrough, the relation $\theta = f(L)$ will change, and for several values of C_1 we will obtain a family of curves of $\theta = f(L)$; these curves correspond to parallel sections of a surface described by the equation

$$C = f(L, \theta);$$

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here C is the concentration at the time θ at the distance L from the beginning of the layer. The curves of $\theta = f(L)$ discussed above show the section of this surface corresponding to constant C . We also need to examine other sections which correspond to constant L or θ . The curves $C = f(\theta)$ are termed the output curves. They show the increase of the concentration behind a layer of length L as a function of time.

Fig. 2. Increase of concentration behind a layer of activated charcoal for three layer lengths $L' < L'' < L'''$

Typical output curves for various values of L are shown in Fig. 2 (from the data of Shilov et al. (Ref. 8)). They show that the shape of the curve depends significantly on the value of L , or, in other words, the larger the value of L , the larger the time interval from the beginning of the operation of an elementary layer located at the distance L until the instant of its saturation.

The curves $C = f(L)$ show the decrease of the concentration of the substance being absorbed for various instants of time along the length of the layer. Relative to the shape of these curves, in the mentioned study of Shilov et al. (Ref. 8) note is made of the "Marked distortion of the entire frontal curve as it advances."

Only in a very rough approximation may we consider that, beginning at some instant of time, the frontal curve advances without changing shape.

In the above phenomenological description of the phenomena, we indicated the approximation which is suitable for a rough description of the part of the experiment corresponding to large values of L .

This estimate with an indication of the roughness of the approximation was formulated by Shilov and his students on the basis of an analysis of experimental material. This estimate corresponds to the pattern of parallel movement of the front. The sense of this approximation amounts to the following.

Beginning at some instant, the frontal curve advances along the sorbent layer without distorting. Then, as a corollary, there must be constancy of the output curves for various values of L and a rectilinear behavior of the relation $\theta = f(L)$. Thus the picture of parallel advance describes very approximately the part of the experiment corresponding to large values of L without considering the initial period of the experiment.

Figure 3 shows the relation $\theta = f(L)$ corresponding to the pattern of parallel advance. Three constants need to be indicated for a quantitative description. Two of the constants determine the position of the line on the plane, and the third determines the length L_0 at which the true rectilinear relation $\theta = f(L)$ begins. Shilov and his students choose these constants as follows.

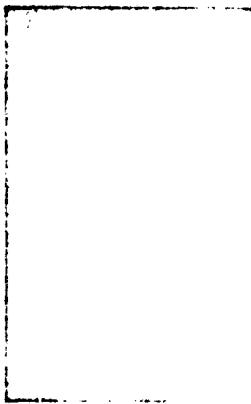


Fig. 3. $\theta = f(L)$ for segment of rectilinear relation

To determine the position of the line on the plane, they selected the slope of the line K and the intercept on the time axis τ (Fig. 3). K is termed the screening effect coefficient. K , equal to $d\theta/dL$, represents the variation of the screening effect with increase of the layer length by 1 cm and has the dimension LT^{-1} . τ is termed the screening action time lag.

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The third constant is denoted by L_0 and represents the length for which parallel advance of the front begins.

Shilov did not give any physical basis for the above scheme. Therefore he was able to present an equation for one of the three indicated constants which may be derived phenomenologically without any physical premises. This pertains to the screening effect coefficient.

Actually, by definition $K = \Delta\theta/\Delta L$.

Here $\Delta\theta$ is the time required for the frontal line to advance over the segment ΔL . Since it is assumed that the front is not altered during the advance, as a result of this advance $S\Delta L \text{ cm}^3$ of charcoal will be saturated.

If the adsorption capacity of unit volume is equal to $a \text{ mg/cm}^3$, then $S\Delta L a \text{ mg}$ are required to saturate this volume. $C_0 V \text{ mg/min}$ of substance enter the layer in unit time, therefore

consequently,

Here $\alpha = V/S$ is the velocity per 1 cm^2 cross-section.

It is to be noted that the equation for K is of practical interest, in spite of the roughness of the approximation used in its derivation.

However the same type of phenomenological derivations cannot be given for τ and L_0 .

The objective of the Necklenburg-Kubelka theory was in essence the determination of τ and L_0 for an approximate representation of sorption dynamics in which parallel advance of the gas front is assumed. But in setting themselves this task, Necklenburg and Kubelka did not formulate the conditions under which parallel advance of the front must take place.

Their physical premises are partially not formulated at all, partially formulated incorrectly, and partially essentially incorrect.

Moreover, as will be shown below, they made mathematical errors which make the equations which they derived meaningless.

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A true theory of sorption dynamics must rest on physical premises relating to three aspects of the phenomenon: statics, kinetics, and aerodynamics of the process.

Statics include the sorption thermal equations. The kinetics relates to the examination of the process which determines the sorption rate. The aerodynamics must represent the gas flow regime in the sorbent layer.

Mecklenburg and Kubelka formulated exactly only the second premise. As the factor which determines the rate of the process they took the diffusion of the gas to the grain. In general, in view of the rapidity of van der Waal adsorption, this premise is reasonable, particularly in light of the experiments of Harned (Ref. 9), who showed that the sorption rate in a vacuum is hundreds of times greater than the sorption rate in the presence of air. Of course, in addition to the diffusion to the grain there may be diffusion through the broad channels of the pores within the grain. However, it may be shown that to a good approximation, with accuracy to a constant, the theory constructed on the assumption of diffusion to the grains also encompasses this process.

With regard to statics, the author really does not examine consistently any single isotherm. The assumption made in the course of the derivation corresponds to the isotherm shown in Fig. 4. The author terms charcoal having this isotherm a "mathematical" adsorbent. From the point of view of capillary condensation this isotherm corresponds to the presence of capillaries of a single radius.

Fig. 4. Isotherm for "mathematical sorbent"

Such a charcoal will not adsorb at all with a concentration less than some value C' . Saturation corresponds to this same concentration. However this isotherm is not analyzed consistently by the authors and the basic premises of Mecklenburg contradict this isotherm. Moreover the authors did not indicate that the theory constructed on this isotherm must correspond to an actual experiment conducted with concentrations lying far in the saturation region.

The third premise amounts to the use of the Nernst equation for describing the diffusion rate:

Here dm is the quantity of gas diffused through the surface F during the time dt ; D is the diffusion coefficient; δ is the thickness of the so-called adhered layer. The concept of the adhered layer is explained in greater detail in the book of Dubinin (Ref. 4) in discussing the Mecklenburg-Kubelka theory: "In spite of the constancy of the linear air flow velocity, near the wall the velocity of the air layers will diminish sharply, so that the air layer in direct contact with the surface of the body will not be in motion" ("internal gas friction phenomenon").

C and C' are the concentrations at the edges of this adhered layer.

Aerodynamics (Ref. 10) considers two basic gas flow regimes -- turbulent and laminar. In both cases there is no motionless gas layer; for laminar motion there is a parabolic velocity distribution across the cross-section of a tube, for turbulent motion there is still a thin laminar layer near the walls. In the case of laminar motion, the diffusion perpendicular to the stream must take place through the entire channel cross-section, in the case of turbulent motion the vortices provide for mixing of the gas within the main part of the channel, and diffusion must take place only through the laminar layer adjacent to the wall. The question then is not the lack of movement or the "retarded" velocity of the gas, as Dubinin writes in Ref. 4, but the absence of vorticity. The thickness of the laminar layer diminishes with the gas linear velocity according to the following empirical law:

here δ and n are empirical constants in the case when the resistance to diffusion lies in the turbulent core. δ is to be understood as the thickness of an equivalent laminar film.

Thus the Mecklenburg-Kubelka "theory" assumes turbulent motion, although the authors did not understand this.

However the variation of the resistance with velocity (Zabeyhinskiy data, Fig. 5) for air velocities through the sorbent layer of practical interest ($\dot{Q} < 1$ liter/min/cm²) is very close to linear. This indicates that the stream is practically laminar. Thus the above premises of Mecklenburg-Kubelka do not correspond to actual experiment.

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Fig. 5. Variation of resistance R in mm H_2O with velocity α (data of Zabzhinskiy)

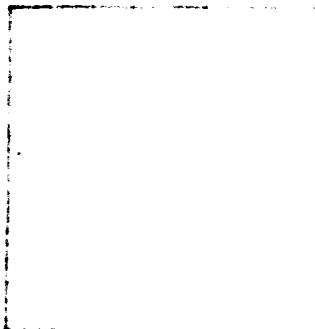


Fig. 6. $\theta = f(L)$ for "mathematical sorbent"

The authors also represent incorrectly the over-all picture of the dynamics in satisfying the assumed physical conditions.

This applies particularly to the relation $\theta = f(L)$. Let us examine the sorption dynamics corresponding to the isotherm which is the basis of the Mecklenburg-Kubelka theory and which is shown in Fig. 4. We can indicate a definite length L_1 at which the breakthrough takes place practically instantaneously. This is the distance covered by the first elementary volume of the gas-air mixture while its concentration is diminishing from C_0 to C_1 . In view of the fact that according to Fig. 4 the equilibrium concentration is constant right up to the instant of saturation, the succeeding elementary volume of the mixture repeats precisely the history of the first. And right up until the saturation of the first elementary layer of the adsorbent the gas front will not advance, and there will be a stationary state in which the gas concentration at any point is independent of time.

After saturation of the first elementary layer the gas front begins to translate with a constant velocity. This picture corresponds to the relation $\theta = f(L)$ shown in Fig. 6.

We see that this curve is quite far from the relation $\theta = f(L)$ obtained experimentally and shown in Fig. 1. This is explained by the difference of the actual isotherm from that which is the basis of the Hecklenburg-Kueelka theory.

The authors of this theory, without explaining the actual pattern of the sorption dynamics on "mathematical charcoal," assume the absence of a stationary period with a fixed gas front and consider that the front advances all the time, and at the instant of saturation of the first elementary layer the length L_0 at which breakthrough occurs is considerably greater than L_1 .

However the equation which they derive (incorrectly) for L_0 actually applies to L_1 , and if they assume $L_0 \gg L_1$ ($S_x \gg S_1$ in Hecklenburg's notation), it cannot in any way be applied to L_0 .

Let us present a natural and correct derivation for L_1 , determining for this the dependence of the concentration on the layer length for the stationary regime. Let us form the vapor balance for a sorbent element located at the distance L from the inlet:

The first two terms give the quantity of vapor which remains in an element of the sorbent layer after the time dt as a result of the presence of the velocity V . The third term represents in accordance with the Nernst equation the quantity of substance which has been diffused to the sorbent in the time dt . D is the diffusion coefficient; F is the surface of unit volume of the adsorbent; $(C - C')/\delta$ is the concentration gradient in the laminar layer.

Let us denote

$$DF/\delta = \beta.$$

We solve Eq. (1), taking into account the boundary condition $C(0) = C_0$,

If the induced concentration is equal to or less than C' , then, as is easily seen, an instantaneous breakthrough will take place at any length. Therefore we shall consider that $C_1 \gg C'$.

Hence

This equation differs from that appearing in the Mecklenburg theory in that in the latter there is the factor $(\alpha/\beta)X$ in place of α/β . Here X is the fraction of the area in the cross-section of the adsorbent corresponding to the spaces between the grains. This is one of the errors of the Mecklenburg-Kubelka "theory." The basic error of Mecklenburg lies in the incorrect form of the basic equation of the "theory." Mecklenburg writes it as follows:

such an equation cannot be written for the unknown C , since C depends only on L and is independent of time.

Let us make the assumption that we are concerned with diffusion from the moving volume ΔW , i.e., the system of coordinates moves with the velocity α/X . But even then this equation is not correct. Actually, following Nernst:

here dm is the quantity of substance which has been diffused; $\Delta W'$ is the volume of the charcoal in contact with the volume being considered; $F\Delta W'$ is the area of this volume.

Then

$$dm = \Delta W' dc;$$

here ΔW is the gas volume being considered.

The following relation exists between ΔW and $\Delta W'$:

$$\Delta W = X \Delta W'.$$

Therefore we obtain in place of the Mecklenburg "equation" the following:

Sequential solution of Eq. (3) leads to the same results as given above (Eq. (2)). However, on the basis of Eq. (2a) Mecklenburg arrives at an incorrect equation describing L_1 .

Mecklenburg quite arbitrarily applies the incorrectly derived equation not to L_1 , which it defines, but to L_0 (in the notation of Mecklenburg, to S_x rather than to S_1), which cannot be done even with equations which are correctly derived.

By this operation Mecklenburg-Kubelka identifies the length of the layer at which instantaneous breakthrough takes place (L_1) with the length of the layer (L_0) beginning with which there is a practically parallel advance of the front, which corresponds to the instant of saturation of the first element of the layer.

We see from Fig. 1 that L_0 is considerably greater than L_1 ($S_x > S_1$ in Mecklenburg's notation). Thus, the equality of L_1 and L_0 which is required by the idealized pattern (Fig. 6) is not satisfied.

In any case, we cannot apply the equation for L_1 to the projection of the point a (Fig. 1). This is the most serious of all the errors of the Mecklenburg-Kubelka "theory." L_0 will depend on the charcoal capacity, which is not the case for L_1 . It was possible to carry out this operation only because an absolute calculation is not made in the Mecklenburg-Kubelka theory; all the constants are combined and are determined from experiment. In this case the application of the equation describing L_1 to L_0 , which exceeds considerably L_0 , leads only to the fact that the experimentally determined constants have un-natural values.

Since the values of F , D , and K may be estimated, there is a possibility of making an absolute calculation of δ_0 (see Eq. 2). In this case δ_0 is greater than the grain diameter, which, of course, is quite meaningless.

This result is quite understandable, since L_1 is proportional to δ_0 , and in order to obtain for L_1 a value which is ten-fold greater it is necessary to overestimate the value of δ_0 tenfold.

The theory of Mecklenburg and Kubelka, constructed on quite unrealistic physical premises, and moreover incorrectly formulated and developed, containing serious mathematical and logical errors, cannot describe experimental results. Agreement with a part of the experimental results may be obtained by introducing empirical constants. In all, five empirically determined constants are introduced in the theory. (In contradiction with the bases of the "theory," which rest on the consideration of the sorption isotherm using a "mathematical sorbent," in the computational equations of the theory there

is introduced the Freundlich isotherm, which has two constants (Ref. 5)).

As a result of such an excess of constants, the dependence of τ on C , V , and d is described only very roughly. In this case the agreement between experiment and "theory" is aided by the free choice of the point at which the rectilinear relation between θ and L begins.

However, such an "empirical" description of the experimental data, first, offers little promise, since it cannot be used to predict, and, second, it must inevitably lead to contradiction with a considerable portion of the experimental data, which is just what happens.

This contradiction lies in the absence of a rectilinear relation $\theta = f(L)$, lack of parallelism of the gas front advance in the sorbent layer, and absence of constant increase of the concentration behind layers of differing length (Shilov (Ref. 8), Bohart and Adams (Ref. 11), and others).

It is of interest that even those who defend the positions of the Mecklenburg theory encounter serious contradictions between experiment and the "theory." Thus, Dubinin and coworkers (Ref. 12) stated that τ and K are dependent on the sensitivity of the gas indication. Both of these quantities clearly diminish with improvement of the indicator. (About by a factor of two in the experiments of Dubinin and coworkers.) However, according to the Mecklenburg theory K must in general not depend on the sensitivity of the indicator. However, unfortunately, this did not cause any natural criticism of the Mecklenburg theory. It is true that a hot discussion arose on the advantages of the notations τ or h ($h = \tau/K$), i.e., essentially on the methods of determining the straight line on the plane. In contradiction to his "theory" Mecklenburg himself noted that with high concentrations the quantity a as determined from experiment (using the formula $K = a/\alpha C_0$) is about 20% less than the value of the equilibrium adsorption capacity. He further noted the dependence of K on d . Finally, for small concentrations (of the order of $4 \cdot 10^{-2}$ mg/liter) deviations from the rectilinear relation of θ with L are noted. Here the curve for large times deviates upward from the straight line, i.e., the experimental times are greater than the calculated times (Fig. 1).

CONCLUSIONS

This paper gives a critical analysis of the basic positions and content of the Mecklenburg "theory." It is shown that this is an erroneous and pseudo-scientific theory.

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